

1,109,787



PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

New Phosphine Derivatives and their use in the Hydroformylation of Olefinic Compounds

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, Holland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the preparation of aldehydes and/or alcohols by reaction of olefins with carbon monoxide and hydrogen in the presence of special phosphine-containing cobalt complexes as catalysts.

The invention also relates to the said special phosphines and the said cobalt complexes and the preparation thereof.

It is already known that complexes comprising cobalt, carbon monoxide and phosphines may be used as catalysts in the preparation of aldehydes and/or alcohols starting from olefins, carbon monoxide and hydrogen. As suitable phosphine components in these complexes trialkylphosphines e.g. tributylphosphine have been proposed.

It has now been found that by selection of heterocyclic phosphines as participants in the catalyst complexes, in which phosphines, a heterocyclic group containing at least five carbon atoms is present, the formation of primary alcohols is promoted and the quantity of saturated hydrocarbons (formed in a side-reaction) is reduced. Furthermore an increase in the hydroformylation rate is observed.

The invention may be defined as relating to a process for the preparation of aldehydes and/or alcohols by reaction of an olefinic compound with carbon monoxide and hydrogen in the presence of a complex catalyst comprising cobalt, carbon monoxide and a phosphine in which reaction the characteristic feature consists in that a catalyst is used which contains a heterocyclic phosphine in which a heterocyclic group with at least five carbon atoms is present.

In their active form, the suitable novel complex catalysts contain the cobalt in a reduced valence state. This will normally be a zero valence state and may suitably be even, lower, such as a -1 valence state. As used throughout this specification and claims, the term "complex" means a coordination compound formed by the union of one or more electronically rich molecules or atoms capable of independent existence with one or more electronically poor molecules or atoms, each of which is also capable of independent existence.

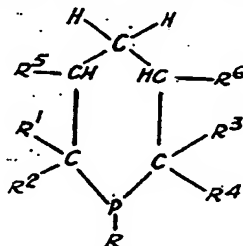
In the special classes of ligands described hereinafter containing trivalent phosphorus comprised in the novel complex catalysts employed in the process of the invention, the phosphorus atom has one available or unshared pair of electrons. When trivalent phosphorus has such an electronic configuration, it is capable of forming a coordinate bond with cobalt in its 0 and -1 valence states. It will thus operate as a ligand in forming the desired novel cobalt complexes used as catalysts in the present invention.

The phosphine ligands may be formed from the compounds described and claimed

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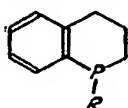
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in specification No. 969,129. These compounds are 4-phosphorinanes of the formula: —

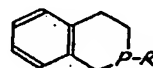


wherein R is a substituted or unsubstituted, branched or straight chain alkyl radical having from 1 to 4 carbon atoms, a phenyl, or 4¹-unsubstituted cycloalkyl radical, or a substituted or unsubstituted aryl radical; each R¹, R², R³ and R⁴ is one of the following; a hydrogen atom, or an alkyl radical containing from 1 to 4 carbon atoms, a phenyl, or 4¹-methyl phenyl radical; and each of R⁵ and R⁶ is a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms; at least one of R¹ to R⁶ being other than a hydrogen atom.

A preferred group of phosphine ligands is formed by the tertiary six-membered heterocyclic phosphines. In these phosphines the phosphorus atom is attached to a hydrocarbyl group and to a 1,5-hydrocarbylene group. By the term "1,5-hydrocarbylene" is meant the diradical formed by removal of one hydrogen atom from each of two different carbon atoms, said carbon atoms being separated by three carbon atoms, of a saturated or unsaturated hydrocarbon containing at least five carbon atoms. Thus, for example, when the 1,5-hydrocarbylene diradical is a pentamethylene, substituted or unsubstituted, the phosphine of the present invention is a phosphorinane. The bridge of 5-carbon atoms, i.e., the 1,5-hydrocarbylene, may be any such radical composed solely of carbon and hydrogen and having a wide variety of alkyl, alkenyl, cycloalkyl, aryl, aralkyl, alkaryl, fused ring, straight chain or branched chain hydrocarbon substituents. Representative substituents on the 1,5-hydrocarbylene diradical include methyl, tertbutyl, hexenyl, isooctyl, decyl, cyclohexyl, phenyl, 1,3-butadienylene, benzyl, phenethyl and styryl groups. It is preferred that any substituent attached to a bridge carbon atom contains no more than 10, preferably no more than 6, carbon atoms and that all such substituents combined contain no more than 40 carbon atoms. It will be understood that when a substituent completes a fused ring for example 1,3-butadienylene, to yield a tetrahydro-phosphinoline



or a tetrahydro-isophosphinoline,



R being (substituted) hydrocarbyl,

it will be considered that each of two adjacent carbon atoms in the 5-carbon atom bridge is substituted once with a 2-carbon substituent. The afore-mentioned substituted 1,5-hydrocarbylene diradicals may also contain a functional group such as the carbonyl, carboxyl, nitro, amino, hydroxy, cyano, sulphonyl and sulphonyl groups.

Thus, for example, when a substituted 1,5-hydrocarbylene diradical is a 3-oxo-1,5-pentamethylene, possibly additionally substituted, the phosphine is a phosphorinane and in the given specific example a 4-phosphorinane. In a preferred group of tertiary, six-membered cyclic phosphines the 1,5-hydrocarbylene diradical contains from 5 to 33 carbon atoms, such that any hydrocarbon substituent attached to a bridge carbon atom of the said diradical contains no more than ten carbon atoms.

The term "hydrocarbyl" is used in its accepted meaning as representing a radical formed from a hydrocarbon by removal of a hydrogen atom. The hydrocarbyl group to which the phosphorus atom is linked may be any organic radical composed solely of carbon and hydrogen. Thus, the hydrocarbyl groups may be alkyl, alkenyl, cycloalkyl, aryl, aralkyl or alkaryl groups. They may contain one or more rings and contain straight or branched chains. Representative hydrocarbyl groups include methyl, ethyl, allyl, n-butyl, hexenyl, isooctyl, dodecyl, octadecyl, eicosyl, triacontyl, cyclohexyl, cyclooctyl, phenyl, naphthyl, benzyl, styryl and phenethyl groups. Substituted hydrocarbyl groups are also operable and may contain one or more functional groups such as carbonyl, carboxyl, nitro, amino, hydroxy (e.g. hydroxyethyl), cyano, sulphonyl,

and sulfoxyl groups. Very suitable are amino-substituted hydrocarbyl groups and especially hydrocarbyl groups substituted by dialkylamino groups wherein each alkyl group contains from 2 to 18 carbon atoms. A preferred group of ligands consists of those in which the said hydrocarbyl group contains from 4 to 36 carbon atoms.

It is sometimes desirable to balance the size of the substituents in the afore-described phosphines. When the substituents of the hydrocarbylene group are numerous and large, it may be desirable to choose a smaller hydrocarbyl group. Conversely, when the hydrocarbyl group is large, e.g. eicosyl or triacontyl, it may be desirable that the hydrocarbylene-substituents be smaller and/or less numerous, such as monomethyl, dimethyl. Particularly useful ligands are those in which the sum of the carbon atoms in the hydrocarbylene and hydrocarbyl groups is no greater than 41 carbon atoms.

Another preferred group of phosphine ligands is formed by the tertiary seven-membered heterocyclic phosphines. In these phosphines the phosphorus atom is attached to a hydrocarbyl group and to a 1,6-hydrocarbylene group. By analogy to the 1,5-hydrocarbylene group the "1,6-hydrocarbylene group" is defined as the diradical formed by removal of one hydrogen atom from each of two different carbon atoms, said carbon atoms being separated by four carbon atoms of a saturated or unsaturated hydrocarbon containing at least six carbon atoms. Thus, for example, when the 1,6-hydrocarbylene diradical is a hexamethylene, substituted or unsubstituted, the phosphine is a phosphepane.

The hydrocarbylene group may be substituted by any one of the groups mentioned hereinbefore as suitable substituents in the bridge of 5 carbon atoms. Preferably it contains from 6 to 34 carbon atoms.

Suitable hydrocarbyl radicals present in the tertiary seven-membered heterocyclic phosphines and containing one or more functional groups as substituents, if so desired, comprise those recommended in the six-membered heterocyclic phosphines. However, in balancing the size of the substituents in the seven-membered ring compounds, it is preferred that the sum of the carbon atoms in the hydrocarbylene and the hydrocarbyl group in the phosphines does not exceed 48.

An especially preferred group of ligands is formed by the bicyclic heterocyclic tertiary phosphines, in particular hydrocarbyl-substituted monophosphabicyclohydrocarbons, saturated or unsaturated, having 8 or 9 ring atoms including the phosphorus atom in which the smallest phosphorus-containing ring contains at least 5 atoms and the phosphorus atom is not a bridgehead atom. In addition to the hydrocarbyl substitution on the phosphorus atom, the ring carbon atoms may also be substituted. However, it is preferred that such substituents be limited to non-bulky ones, such as in particular, alkyl groups with 1 to 4 carbon atoms. It is recommended that no more than two alkyl substituents are present at the same time and that these are attached to different ring carbon atoms.

The aforesaid monophosphabicyclo hydrocarbons suitably contain from 7 to 46 carbon atoms and preferably from 12 to 40 carbon atoms.

Very suitable are bicyclic tertiary phosphines unsaturated in the bicyclic portion of the ligand, in particular the hydrocarbyl-substituted monophosphabicyclo nonatrienes. In these ligands the total number of carbon atoms is usually from 8 to 44 and preferably from 12 to 38.

In the bicyclic heterocyclic tertiary phosphines the hydrocarbyl group and substituents therein if any may suitably be selected from the hydrocarbyl groups and functional groups mentioned above in connection with the monocyclic phosphines. Preferably the hydrocarbyl group contains from 1 to 36 and in particular from 4 to 30 carbon atoms.

The tertiary, six-membered heterocyclic phosphines and their preparation are well described by Maier, L., "Progress in Inorganic Chemistry", Vol. 5, F.A. Cotton, ed., Interscience Publishers, N.Y., 1963, pp. 167—170, 175—177, and by Mann, F.G., "Progress in Organic Chemistry", Vol. 4, F.W. Cook, ed., Butterworths, London, 1958, p. 224—226.

Seven-membered heterocyclic tertiary phosphines with no ring carbon substituents may be prepared according to U.S. Specification 3,086,053 by reaction of hexamethylene dihalides with monosubstituted alkali metal derivatives of primary phosphines in a liquid ammonia medium.

A preferred method for the production of 6- and 7-membered heterocyclic tertiary phosphines by a practical one-stage process consists in reacting divinyl-substituted hydrocarbons containing two non-conjugated double bonds with monosubstituted, i.e. primary, phosphines in the presence of a free radical-generating catalyst and in the absence of substantial amounts of oxygen.

Suitable divinyl-substituted hydrocarbons are dienes in which the double bonds are isolated, i.e. non-conjugated double bonds. A particularly useful class of divinyl-substituted hydrocarbons is that represented by the formula $Q(CR'=CH_2)_2$, in which Q represents a hydrocarbylene group wherein the connecting-bridge moiety always has from 1 to 2 carbon atoms in the bridge between the vinyl groups and R' represents either hydrogen or a lower alkyl group having 1 to 5 carbon atoms, preferably a methyl, ethyl, propyl or butyl group. Hydrocarbylene groups wherein the connecting bridge moiety always contains from 1 to 2 vinyl-bridging carbon atoms are fundamentally methylene and ethylene divalent radicals, either unsubstituted or substituted with a wide variety of alkyl, alkylene, cycloalkyl, aryl, aralkyl, alkaryl, straight chain or branched chain, hydrocarbon substituents and structures. Representative hydrocarbyl substituents include methyl, tert-butyl, cyclohexyl, decyl, octadecyl, phenyl, benzyl, phenethyl. It is preferred that any substituent attached to a bridge carbon atom contains no more than 10, preferably no more than 6, carbon atoms, and that all such substituents contain no more than a total of 20 carbon atoms. Thus, a preferred group of divinyl-substituted hydrocarbons contains those represented by the formula $Q(CR'=CH_2)_2$ in which Q represents a hydrocarbylene group of from 1 to 14 carbon atoms, with the proviso that the bridge moiety is a bridge of 1 to 2 carbon atoms and that any hydrocarbon substituent attached to a bridge carbon atom contains no more than 10 carbon atoms, and R' represents hydrogen or a lower alkyl group having 1 to 5 carbon atoms. Representative examples of these divinyl hydrocarbons include 1,4-pentadiene, 3-methyl-1,4-pentadiene, 2,4-dimethyl-1,4-pentadiene, 3,3-dimethyl-1,4-pentadiene, 2,3,4-trimethyl-1,4-pentadiene, 3-phenyl-1,4-pentadiene, 3,3-diphenyl-1,4-pentadiene, biallyl, bimethallyl, 3-phenyl-1,5-hexadiene or 3,4-dimethyl-1,5-hexadiene. Preferred are 1,4-pentadiene, 3,3-dimethyl-1,4-pentadiene, biallyl, and bimethallyl.

The monosubstituted phosphine to be started from has the formula RPH_2 in which R represents a hydrocarbyl group. A preferred group of primary phosphines consists of those in which R is a hydrocarbyl group of from 1 to 36 carbon atoms, and especially preferred are those in which the hydrocarbyl group contains from 4 to 30 carbon atoms.

The cyclization reaction is carried out with the aid of a free radical-generating catalyst, such as an azonitrile, or a dialkyl or diacyl peroxide. The term "free radical-generating catalyst" is also meant to include actinic radiation, particularly ultraviolet light, and high-energy or ionizing radiation such as use of cobalt-60, a source of high-energy γ or X rays. The azonitrile catalysts which may be employed in this reaction are well known in the art and include α , α' -azobisisobutyronitrile; α , α' -azobis (α -methylbutyronitrile) or α , α' -azobis (α -methyl-isocapronitrile). Suitable peroxide catalysts include the dialkyl peroxides such as di(tert-butyl) peroxides, and the diacyl peroxides such as butyryl, lauroyl, and benzoyl peroxides. The amount of catalyst which may be used may vary over a wide range from 0.1% by weight upward. From 0.5 to 5% by weight of catalyst, based on the weight of the mono-substituted phosphine reactant, is ordinarily desirable. The dialkyl peroxides represent a preferred class of catalysts owing to their unusual stability during handling.

The two reactants may be used in equimolecular amounts or in a slight molar excess of one reactant or the other. In a preferred mode of operation the reactants are used in equimolar quantities to maximize the cyclization. The reaction may be conducted in the presence of a non-reactive solvent medium such as aliphatic cyclic and acyclic saturated hydrocarbons, e.g. pentane, n-hexane, cyclohexane, petroleum ether or isooctane. It is sometimes desirable, for example, when the molecular weights of the reactants are low, to conduct the cyclization in the presence of one of the aforesaid solvents in orders to dilute the reactants, thereby maximizing cyclization and minimizing polymerization. Such solvents also aid in dissipating the heat generated in this exothermic reaction. The mixture and its environment should be free of substances capable of converting the tert-phosphines to the corresponding phosphine oxides, such as oxygen and air. Hence, the reaction should be conducted in an inert atmosphere such as under nitrogen or, when the reactants are sufficiently high-boiling, under vacuum. If desired, small amounts of oxidation inhibitors optionally may be used.

The temperature at which the reaction should be conducted will be governed by the specific catalyst employed in that a useful temperature is one at which the free radical-generating catalyst decomposes or furnishes free radicals at a moderately even rate throughout the course of the reaction. For example, when the free radical-

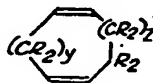
generating is actinic radiation, particularly ultraviolet, at ambient room temperature is sufficient. When α , α' -azobisisobutyronitrile is the catalyst, a temperature of about 70°C, conveniently obtained by conducting the reaction in refluxing n-hexane, is sufficient. On the other hand, when the free radical-generating catalyst is a dialkyl peroxide, temperatures of 110–150°C will be desired in order to decompose smoothly the peroxide. The cyclization may be carried out at any temperature short of the rapid decomposition point of any of the catalysts used. The lower temperature limit is that at which the condensation becomes impractically slow. Temperatures from –10° to 200°C may be used, the preferred range being from 15°C to 175°C. The reaction will usually be carried out at just above atmospheric pressure, although higher or lower pressures may be used, with due consideration given to the physical properties of the reactants, e.g. volatility and the like, as mentioned previously.

Only one compound which contains a 7-membered, ring carbon-substituted, phosphorus-containing ring (i.e. 10,11-dihydro-5H-5-phenyl-dibenzo[*b,f*]phosphepin or 1-phenyl-1-phospha-2,3,6,7-dibenzo-2,6-cycloheptadiene) has been reported in the literature (F.G. Mann et al, J. Chem. Soc., 1953, 1130).

The novel heterocyclic tertiary-phosphines prepared as described hereinbefore, are colourless liquids, and particularly those containing less than 20 carbon atoms, are rather malodorous. The higher boiling ones, for example those containing more than 20 carbon atoms, have less odour and tend to crystallize upon standing to yield waxy materials which melt in the range of about 40–60°C. They are also relatively stable to oxidation upon standing.

A preferred method for the preparation of novel bicyclic heterocyclic secondary and tertiary phosphines consists in reacting certain phosphines with suitable cyclic diolefinic compounds in the presence of a free radical-generating catalyst and in the absence of substantial amounts of oxygen. In a preferred one-step method, the aforesaid bicyclic compounds are produced by reacting a cyclic hydrocarbon containing two ring non-conjugated and non-homoconjugative double bonds with phosphine (PH₃) or monosubstituted, i.e. primary, phosphine in the presence of a free radical-generating catalyst and in the absence of substantial amounts of oxygen. The method is in particular suitable for the preparation of novel bicyclic heterocyclic tertiary phosphines.

Recommended cyclic hydrocarbons are cyclic dienes in which the double bonds not only are isolated, i.e. non-conjugated double bonds, but also are non-homoconjugative double bonds, i.e., non-conjugated systems which do not behave as conjugated systems. A particular useful class of cyclic hydrocarbons is that represented by the formula



where y and z represent positive integers whose sum is from 2 to 3 and each of which has a minimum value of 1, and R may be either hydrogen or a lower alkyl group of from 1 to 4 carbon atoms such that not more than two alkyl groups are present at the same time and that these alkyl groups are attached to different ring carbon atoms. Representative examples of these cyclic dienes include 1,5-cyclooctadiene, 3,7-dimethyl-1,5-cyclooctadiene, 3,8-dimethyl-1,5-cyclooctadiene, 1,4-cycloheptadiene or 6-methyl-1,4-cycloheptadiene. Preferred are 1,5-cyclooctadiene and 3,7-dimethyl-1,5-cyclooctadiene. Larger ring compound starting reactants are not preferred because the cyclization reaction operates most favourable when the bicyclic rings formed are 5-, 6-, and 7-membered rings. It is to be understood that cyclic conjugated dienes and cyclic non-conjugated homoconjugative dienes are inoperable. Examples of such conjugated dienes include 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, and the like. Cyclic non-conjugated homoconjugative dienes include 1,4-cyclohexadiene, bicyclo[2.2.1]hepta-2,5-diene (a bridged 1,4-cyclohexadiene), and the like. Such reagents do not yield the novel cyclization reaction but react with one hydrogen atom of the primary phosphine reactant in a conventional 1,4-addition known to the prior art to yield a resulting secondary, i.e. disubstituted, phosphine.

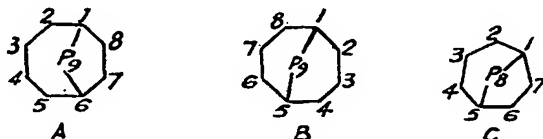
The phosphine to be used is either phosphine (PH₃) itself, or a monosubstituted phosphine, i.e. primary organic phosphine, containing a hydrocarbyl group. Repre-

sentative hydrocarbyl groups have been mentioned before and contain preferably from 1 to 36 carbon atoms, and in particular from 4 to 30 carbon atoms.

The cyclization reaction may suitably be carried out in the same way as hereinbefore described for the preparation of 6- and 7-membered heterocyclic tertiary phosphines.

An alternative method by which the novel bicyclic heterocyclic tertiary-phosphines can be produced is a two-step process. In the first step, the hereinabove described cyclic dienes in the presence of a free radical-generating catalyst and in the absence of substantial amounts of oxygen undergo the cyclization process with phosphine (PH_3) to produce the aforesaid novel bicyclic heterocyclic secondary-phosphine. Optionally without further isolation, the secondary-phosphine is reacted in the presence of a free radical-generating catalyst with a cyclic or non-cyclic compound containing at least one ethylenically unsaturated linkage, e.g. a (cyclic) olefin or diolefin, to produce the tertiary-phosphine. For example, phosphine (PH_3) and 1,5-cyclooctadiene can be cyclized to give the corresponding bicyclic secondary-phosphine; then cyclooctene or cyclododecene or even additional cyclooctadiene may be added as the ethylenically unsaturated reagent to yield in the second step a cyclic-substituted bicyclic tertiary phosphine. Phosphine (PH_3) made by various methods, for example that made by chemical or electrochemical methods, and in different degrees of purity may be utilized in this alternative method. Such a reaction sequence as described hereinabove lends itself well to commercial processing and is economically feasible and attractive. An additional advantage is the elimination of difficult preparations of monosubstituted (primary) phosphines, particularly in the case of long-chain alkylphosphines such as eicosylphosphine.

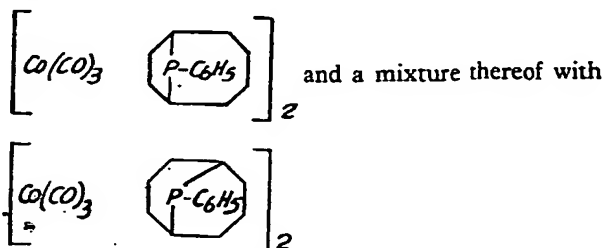
It will be apparent from the preceding discussion that a variety of substituted and unsubstituted monophosphabicycloalkanes may be produced. In the nomenclature of such compounds, as well as the reactants employed for the production thereof, conventional numbering of the ring systems has been employed, as further illustrated by the following formulas:



Typical products numbered according to this system include 9-phosphabicyclononanes in which the smallest P-containing ring contains at least 5 atoms; e.g. 9-phosphabicyclo[4.2.1]nonane; 9-phosphabicyclo[3.3.1]nonane; 9-hydrocarbyl-9-phosphabicyclononanes in which the smallest P-containing ring contains at least 5 atoms; e.g. 9-hydrocarbyl-9-phosphabicyclo[4.2.1]nonane; 9-aryl-9-phosphabicyclo[4.2.1]nonanes such as 9-phenyl-9-phosphabicyclo[4.2.1]nonane; (di)alkyl-9-aryl-9-phosphabicyclo[4.2.1]nonanes such as 3,7-dimethyl-9-phenyl-9-phosphabicyclo[4.2.1]nonane and 3,8-dimethyl-9-phenyl-9-phosphabicyclo[4.2.1]nonane; 9-alkyl-9-phosphabicyclo[4.2.1]nonanes; such as 9-octadecyl-9-phosphabicyclo[4.2.1]nonane, 9-hexyl-9-phosphabicyclo[4.2.1]nonane, 9-eicosyl-9-phosphabicyclo[4.2.1]nonane, and 9-triacontyl-9-phosphabicyclo[4.2.1]nonane; 9-cycloalkyl-9-phosphabicyclo[4.2.1]nonanes; such as 9-cyclohexyl-9-phosphabicyclo[4.2.1]nonane; 9-hydrocarbyl-9-phosphabicyclo[3.3.1]nonanes; 9-aryl-9-phosphabicyclo[3.3.1]nonanes, such as 9-phenyl-9-phosphabicyclo[3.3.1]nonane; 9-alkyl-9-phosphabicyclo[3.3.1]nonanes, such as 9-hexyl-9-phosphabicyclo[3.3.1]nonane and 9-eicosyl-9-phosphabicyclo[3.3.1]nonane; (di)alkyl-9-aryl-9-phosphabicyclo[3.3.1]nonanes such as 3,7-dimethyl-9-phenyl-9-phosphabicyclo[3.3.1]nonane and 3,8-dimethyl-9-phenyl-9-phosphabicyclo[3.3.1]nonane; 9-cycloalkyl-9-phosphabicyclo[3.3.1]nonanes, such as 9-cyclohexyl-9-phosphabicyclo[3.3.1]nonane; 8-phosphabicyclo[3.2.1]octane; 8-hydrocarbyl-8-phosphabicyclo[3.2.1]octanes; 8-aryl-8-phosphabicyclo[3.2.1]octanes such as 8-phenyl-8-phosphabicyclo[3.2.1]octane; alkyl-8-aryl-8-phosphabicyclo[3.2.1]octanes such as 6-methyl-8-phenyl-8-phosphabicyclo[3.2.1]octane; 8-alkyl-8-phosphabicyclo[3.2.1]octanes such as 8-butyl-8-phosphabicyclo[3.2.1]octane, 8-eicosyl-8-phosphabicyclo[3.2.1]octane, 8-triacontyl-8-phosphabicyclo[3.2.1]octane, and 8-octadecyl-8-phosphabicyclo[3.2.1]octane.

It is to be understood that the suitable novel catalysts being novel complexes

between cobalt, carbon monoxide, and phosphine ligand may be monomeric in structure or may be composed of several monomeric units. Thus, the novel complex may be present as a dimer. A particularly preferred catalyst comprises cobalt-tricarbonyl-9-phenyl-9-phosphabicyclo[4.2.1]-nonane, belived to be dimeric



The novel catalysts can be prepared by a diversity of methods. A convenient method is to combine a cobalt salt, organic or inorganic, with the desired phosphine ligand in liquid phase. Suitable cobalt salts comprise, for example, cobalt carboxylates such as acetates and octanoates, as well as cobalt salts of mineral acids such as chlorides, fluorides, sulphates and sulphonates. Also recommended are mixtures of these cobalt salts. It is preferred, however, that when mixtures are used, at least one component of the mixture be a cobalt alkanoate of 6 to 12 carbon atoms. The valence state of the cobalt may then be reduced and the cobalt-containing complex formed by heating the solution in an atmosphere of hydrogen and carbon monoxide. The reduction may suitably be performed prior to the use of the catalysts or it may be accomplished simultaneously with the hydroformylation process in the hydroformylation zone. According to another suitable embodiment the novel catalysts are prepared from a carbon monoxide complex of cobalt. For example, it is possible to start with di-cobalt octacarbonyl and, by heating this substance with a suitable phosphine ligand of one of the classes previously described, to replace one or more of the carbon monoxide molecules, thus producing the desired catalyst. When this latter method is executed in a hydrocarbon solvent, the complex may be precipitated in crystalline form by cooling the hot hydrocarbon solution. X-ray analyses of the isolated crystalline solid show the crystalline form of the complex to be a dimer with a linear P—Co—Co—P group in the molecule. This method is very convenient for regulating the number of carbon monoxide molecules and phosphine ligand molecules in the catalyst. Thus, by increasing the proportion of phosphine ligand added to the dicobalt octacarbonyl, more of the carbon monoxide molecules are replaced.

In accordance with the invention, olefinic compounds are hydroformylated to reaction products predominating in primary alcohols by intimately contacting the olefinic compound in liquid phase with carbon monoxide and hydrogen in the presence of the above-defined catalysts.

A particular advantage of the process of the invention resides in the catalyst's stability and its high activity for long periods of time at very low pressures. Consequently, hydroformylation in accordance with the present invention may be carried out at pressures well below 68 atmospheres to as low as 1 atmosphere or less. Under comparable conditions, known catalysts such as dicobalt octacarbonyl, often decompose and become inactive. The invention is, however, not limited in its applicability to the lower pressures and pressures in the broad range from atmospheric up to 136 atmospheres and higher, e.g. up to 340 atmospheres, may be employed. The specific pressure preferably used will be governed to some extent by the specific charge and catalyst employed, as well as equipment requirements. In general, pressures in the range of from 20.4 to 102 atmospheres and particularly in the range of from 27.2 to 81.6 atmospheres are preferred. The unique stability of the catalysts of the present invention at the lower pressures makes the use of pressures below 102 atmospheres particularly advantageous.

Temperatures employed will generally range between 100°C and 300°C and preferably between 125°C and 210°C, a temperature between 150°C and 200°C being generally satisfactory. Somewhat higher or lower temperatures may, however, be used.

The ratio of catalyst to the olefinic compound to be hydroformylated is generally not critical and may vary widely. It may be varied to achieve a substantially homogeneous reaction mixture. Solvents are therefore not required. However, the use of solvents which are inert, or which do not interfere to any substantial degree with the desired hydroformylation reaction under the conditions employed, may be used.

Saturated liquid hydrocarbons, for example, may be used as solvent in the process, as well as alcohols, ethers, acetonitrile and sulfolane. Molar ratios of catalyst to olefinic compound in the reaction zone at any given instant between 1 : 1000 and 10 : 1 are found to be satisfactory; higher or lower catalyst to olefinic compound ratio may, however, be used, but in general it will be less than 1 : 1.

The ratio of hydrogen to carbon monoxide charged may vary widely as well. In general, a mole ratio of hydrogen to carbon monoxide of at least 1 : 1 is employed. Suitable ratios of hydrogen to carbon monoxide comprise those within the range from 1 : 1 to 10 : 1. Higher or lower ratios may, however, be employed. The ratio of hydrogen to carbon monoxide employed will be governed to some extent by the nature of the reaction product desired. If conditions are selected that will result primarily in an aldehyde product, only one mole of hydrogen per mole of carbon monoxide enters into reaction with the olefinic compound. When the primary alcohol is the preferred product as in the present invention, two moles of hydrogen and one mole of carbon monoxide react with each mole of olefinic compound. The use of ratios of hydrogen to carbon monoxide which are somewhat higher than those defined by these stoichiometrical values are generally preferred.

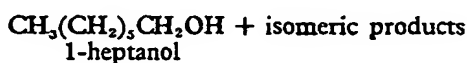
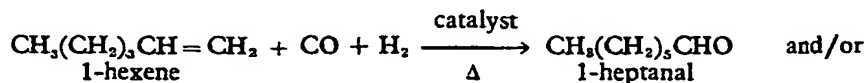
A signal advantage of the present invention as indicated above and further evidence by the following examples is the ability to effect the direct, single-stage hydroformylation of the olefinic compounds to a reaction mixture wherein primary alcohols predominate over the aldehydes and by-product saturated hydrocarbons. The alcohols obtained from the starting olefins are furthermore generally primarily the straight chain or normal isomers. By selection of reaction conditions within the above-defined range, it is now possible to obtain a predominant portion of the product in the form of the normal or straight-chain compound rather than as its various branch-chain isomers. Generally, the alcohol is the desired end product and the catalysts defined herein will produce this product under a relatively wide range of conditions. However, by varying the operating conditions within the range described herein, the ratio of aldehyde to alcohol product may be varied somewhat. Adjustment of these variables also permits some control over the particular isomer that will be produced.

The process of this invention is generally applicable to the hydroformylation of any aliphatic or cycloaliphatic compound having at least one aliphatic carbon-to-carbon unsaturation, especially an ethylenic carbon-to-carbon bond. Thus, it is applied to the hydroformylation of olefins having, for example, from 2 to 19 carbon atoms to yield reaction mixtures predominating in aliphatic aldehydes and alkanols having one or more carbon atom than the starting olefin. The invention is used to advantage in the hydroformylation of carbon-to-carbon ethylenically unsaturated linkages in hydrocarbons. Monoolefins such as ethylene, propylene, butylene, cyclohexene, 1-octene, dodecene, 1-octadecene and dihydronaphthalene are a few examples of suitable hydrocarbons. Suitable hydrocarbons include both branched- and straight-chain, as well as cyclic, compounds having one or more of these ethylenic or olefinic sites. These sites may be conjugated, as in 1,3-butadiene, or non-conjugated, as in 1,5-hexadiene and 1,5-bicyclo[2,2,1]heptadiene. In the case of polyolefins, it is possible to hydroformylate only one of the olefinic sites or several or all of these sites. The unsaturated carbon-to-carbon olefinic linkages may be between terminal and their adjacent carbon atoms, as in 1-pentene, or between internal chain carbon atoms, as in 4-octene.

Olefinic hydrocarbon fractions, such as, for example, polymeric olefinic fractions, cracked wax fractions, and the like containing substantial proportions of internal olefins are readily hydroformylated to fractions of hydroformylated products comprising mixtures of terminal aldehydes and alcohols having one more carbon atom than the olefins in the charge and wherein these primary alcohols are the predominant reaction product. Such suitable feeds consisting of olefinic hydrocarbon fractions include, for example, C_7 , C_8 , C_9 , C_{10} and higher olefinic fractions as well as olefinic hydrocarbon fractions of wider boiling ranges such as C_{7-9} , C_{10-13} , C_{14-17} olefinic hydrocarbon fractions.

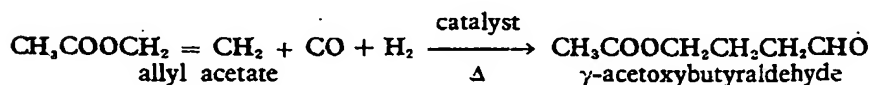
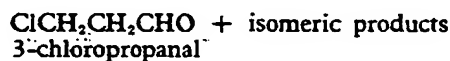
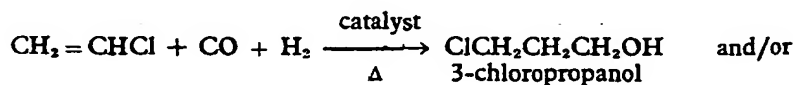
The process and novel catalysts according to the invention may also be used to hydroformylate ethylenic carbon-to-carbon linkages of non-hydrocarbons. Thus, it is possible to hydroformylate olefinically unsaturated alcohols, aldehydes, and acids to corresponding alcohols, aldehydes, and acids containing an aldehyde or hydroxy group on one of the carbon atoms previously involved in the olefinic bond of the starting material; unsaturated aldehydes yield principally diols. The following are a

few specific examples of different types of olefinic compounds that may be hydroformylated in accordance with the invention and the products obtained thereby.



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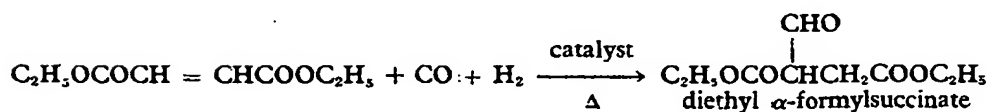
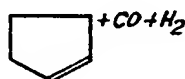
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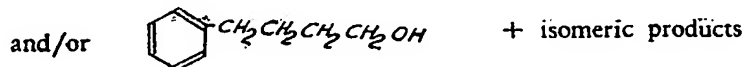
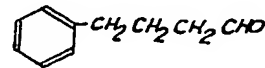
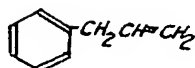
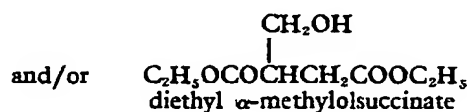


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The olefinic charge may comprise two or more of the above-defined suitable olefins. Olefinic hydrocarbon fractions are hydroformylated under the conditions above-defined to mixtures of aldehydes and alcohols in which the alcohols predominate.

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The reaction mixtures obtained may be subjected to suitable catalyst and product separating operations comprising one or more such steps, for example, as stratification, solvent extraction, distillation, fractionation, adsorption, etc. Catalysts, or components thereof, as well as unconverted charge, may be recycled in part or entirely to the reaction zone.

EXAMPLES I—VI

In Table I some reaction conditions and results are tabulated concerning the preparation of 6- and 7-membered heterocyclic phosphines.

EXAMPLE VII

A 1-litre Morton flask fitted with stirrer, condenser, thermometer, and dropping funnel was charged with 225 g (0.81 mole) of eicosylphosphine and 90 g (0.82 mole) of bimethallyl. The flask was previously purged with nitrogen and a nitrogen blanket was maintained. The reactants were heated to 135° by means of an oil bath. A sample was removed and its infrared spectrum recorded. A solution of 6 g (0.041 mole) of di(tert-butyl) peroxide in 25 ml of n-decane was added dropwise over a period of 45 minutes, the temperature being maintained at 135—145°C. Initially the reaction was exothermic and the temperature was controlled by temporarily lowering the oil bath. After the addition of peroxide was completed, the mixture was held at 150°C for 1-3/4 hours and a sample was then withdrawn. The infrared spectrum showed that the olefinic bands originally present at 6.1 and 5.65 μ had disappeared although —PH absorption at 4.45 μ was still quite pronounced. Heating at 150°C for one additional hour did not result in significant change in —PH absorption. The reaction mixture was then distilled to give 26 g of unreacted eicosylphosphine, b.p. 161—170°C at 0.5 mm, and 249.5 g of 1-eicosyl-3,6-dimethylphosphpane, b.p. 226—236°C at 0.3—0.5 mm. The 1-eicosyl-3,6-dimethylphosphpane crystallized, melting at 47—48°C, and was further identified by elemental analysis.

Analysis

Calculated for $C_{28}H_{54}P$: C 79.2; H 13.5; P 7.3;

Basicity: 0.24 eq/100 g.

Found : C 79.7; H 13.8; P 7.3;

Basicity: 0.22 eq/100 g.

EXAMPLE VIII

A 500 ml reactor flask fitted with stirrer, thermometer, reflux condenser, dropping funnel and nitrogen inlet was charged with 81 grams (0.75 mole) of redistilled 1,5-cyclooctadiene and 83 grams (0.75 mole) of phenylphosphine. A nitrogen blanket was maintained at all times. A sample was then removed and its infrared spectrum recorded. The temperature of the reaction mixture was raised to 135°C by means of an oil bath, and a solution of 2.8 grams (0.019 mole) of di(tert-butyl)peroxide in

TABLE I

Starting materials	Solvent etc.	Further experimental data	Conversion	Product	Yield	Conditions applied in the product isolation	Analysis of the product
Phenylphosphine 7.0 gr (0.064 mole) 1,4-pentadiene 4.3 gr (0.072 mole)	deaerated pentane 75 ml	pyrex glass polymerization bottle. Flushed with N ₂ . 7 Days in sunny location at ambient temp.		1-phenylphosphorinane	4.2 gr. (39%)	distillation at 0.5—1 mm b.p. 85—75°C.	Via crystalline methiodide (m.p. 172—173°C.) Calc. for C ₁₂ H ₁₈ PI: C 45.0; H 5.7; I 39.6 Found: C 44.9; H 5.8; I 39.1
Phenylphosphine 22 gr. (0.2 mole) 3,3-dimethyl-1,4-pentadiene 19 gr. (0.2 mole)	deaerated pentane 250 ml.	pyrex glass polymerization bottle. Two weeks in sunlight	42%	4,4-dimethyl-1-phenylphosphorinane	17.2 gr. (94%)	distillation at 1 mm b.p. 105—107°C. still residue 2.5 gr.	Calc. for C ₁₃ H ₁₈ P: C 75.7; H 9.3; P 15.0 Found: C 74.9; H 9.2; P 14.6 via methyliodide melting at 195—196°C. Calc. for C ₁₄ H ₂₂ PI: C 48.3; H 6.4; P 8.9; I 36.4 found: C 48.3; H 6.3; P 8.4; I 36.2;
Phenylphosphine 22 gr (0.2 mole) bimethallyl 22 gr (0.2 mole)	degassed pentane 700 ml	1 L flask under N ₂ , stirred 119 h irradiated with mercury lamp (GEH 100 A ₄) glass envelope removed placed in centre neck of flask	38%	3,6-dimethyl-1-phenylphosphorinane	16.6 gr. (90%)	distillation at 8 mm b.p. 160—162°C. still residue 4.2 gr	Calc. for C ₁₄ H ₂₁ P: C 76.3; H 9.6; basicity 0.45 eq/100 gr Found: C 76.1; H 9.6; basicity 0.45 eq/100 gr Structure confirmed by NMR spectrography

TABLE 1 (continued)

Starting materials	Solvent etc.	Further experimental data	Conversion	Product	Yield	Conditions applied in the product isolation	Analysis of the product
Phenylphosphine 11 gr. (0.1 mole) bimethallyl 11 gr. (0.1 mole)	n-hexane 150 ml azobisisobutyronitrile 1.64 gr	48-reflux under N_2 blanket after 24 h second half of azobisisobutyronitrile was added.	57%	3,6-dimethyl-1-phenylphosphine	12.5 gr. (83%)	solvent stripped vacuum distillation at 1.5 mm b.p. 120—130°C. still bottoms 3.7 gr.	not analysed
Phenylphosphine 11 gr. (0.1 mole) biallyl 8 gr. (0.1 mole) Octadecylphosphine 29 gr. (0.1 mole) bimethallyl 11 gr. (0.1 mole)	pentane 55 ml de-gassed hexane 150 ml.	pyrex glass polymerization bottle. 11 days in sunlight stirred and irradiated for 7 days at 20°C. with mercury lamp in water cooled quartz thimble	90%	1-phenylphosphine 3,6-dimethyl-1-octadecylphosphine	4.8 gr. 20 gr. (35%)	distillation at 0.2 mm b.p. 88—92°C. 2.0 gr unknown fraction b.p. 195—215°C. at 0.2 mm. 10.4 gr. still residue distillation at 0.9 mm b.p. 223—225°C. still residue 11.3 gr. 5.2 gr. unreacted octadecylphosphine b.p. 125—135°C. at 0.9 mm	via methiodide mp. 131—132°C. Calc. for $C_{13}H_{20}P$: 46.7; H 6.0; P 9.30; I 38. Found: C 46.7; H 6.1; P 9.5; I 37.5 Calc. for $C_{28}H_{50}P$: C 78.7; H 13.5. Found: C 78.4; H 13.4

- 10 ml of n-octane added at such a rate as to maintain the temperature at 135—145°C. The exothermic reaction was controlled by lowering the oil bath as necessary; the addition required 50 minutes. The mixture was then held at 150°C for one hour. Another portion of di(tert-butyl)peroxide, equal to that above, was then added rapidly and the mixture held at 150°C for one additional hour. The infrared spectrum indicated that olefinic bands at 6.1 and 4.4 μ had disappeared. The reaction mixture was then distilled through a 6-inch Vigreux column to give 138 grams (84%) of a mixture of 9-phenyl-9-phosphabicyclo[4.2.1]nonane and 9-phenyl-9-phosphabicyclo[3.3.1]nonane, b.p. 134—135°C at 0.3 mm. Still residue amounted to 15.3 grams.
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- 10
- Analysis: Calculated for $C_{14}H_{18}P$: Basicity 0.46 eq/100 g.
Found: Basicity 0.43 eq/100 g.
- Gas chromatographic analysis (6-ft silicone rubber column, 225°C) demonstrated the presence of two closely eluted isomers in the ratio of 1.99:1. On standing for several days at ambient temperature this material partially crystallized. The crystals were separated from the mother liquor by filtration in an atmosphere of nitrogen. Two sublimations (at 0.5 mm) from an oil bath at 70°C afforded analytically pure 9-phenyl-9-phosphabicyclo[3.3.1]nonane, m.p. 85.5—86.5°C, the isomer eluting later in the gas chromatographic analysis.
- 15
- Analysis: Calculated for: $C_{14}H_{18}P$: C 77.0; H 8.8; P 14.2;
Found: C 76.9; H 8.9; P 14.5.
- 20
- Gas chromatographic analysis of the mother liquor showed that the ratio of earlier, i.e. 9-phenyl-9-phosphabicyclo[4.2.1]nonane, to later eluting isomer had increased to 3.66:1. The structural assignment of the isomers is based on mass spectral data.
- 25
- EXAMPLES IX—XI
- The preparation of bicyclic heterocyclic phosphines is further illustrated by the experiments, results of which are collected in Table II.

TABLE II

Starting materials	Solvent etc.	Further experimental data	Conversion	Product	Yield	Conditions applied in the product isolation	Analysis of the product
Phenylphosphine 22 gr. (0.2 mole) 1,5-cyclooctadiene 22 gr. (0.2 mole)	deaerated hexane 150 ml.	8 days irradiated with mercury lamp at two inches (glass envelope removed)	71%	9-phenyl-9-phosphabicycnonanes	31.4 gr. (94%)	solvent removed distillation through 6" Vigreux b.p. 123—127 °C. still residue 2.4 gr.	Shown by gas chromatography that ratio [4.2.1]nonane to [3.3.1]nonane was 1.91:1 via ethiodide m.p. 277—278 °C.(dec) Calc. for $C_{18}H_{28}P$: C 51.4; H 6.5; P 8.3; I 33.9 Found: C 51.5; H 6.5; P 8.5; I 34.0
Phenylphosphine 22 gr. (0.2 mole) 1,5-cyclooctadiene 22 gr. (0.2 mole)	de-gassed hexane 150 ml.	64 h irradiated with γ -radiation from Co^{60} source at ambient temp. dose 1 Mrad/hr.	68%	9-phenyl-9-phosphabicycnonanes	27.8 gr. (95%)	distillation through 6" Vigreux b.p. 126—132 °C. at 0.3—0.4 mm still residue 2.0 gr.	not analysed
9-phosphabicycnonanes 27.4 gr. (0.19 mole) 1-hexene 84 gr. (1.0 mole)	azobisisobutyronitrile 1.65 gr. (0.01 mole)	29 hr heated under reflux in N_2 atmosphere		9-hexyl-9-phosphabicycnonane [4.2.1]nonane and 9-hexyl-9-phosphabicycnonane [3.3.1]nonane	30 gr. (69%)	excess hexene stripped off distillation through 6" Vigreux b.p. 122—125 °C. at 0.5 mm still residue 5.9 gr.	Calc. for $C_{14}H_{22}P$: C 74.3; H 12.0; basicity 0.44 eq/100 gr. Found: C 74.5; H 12.0; basicity 0.43 eq/100 gr.

EXAMPLE XII

A 500 ml Morton flask fitted with stirrer, thermometer, condenser and dropping funnel was purged with nitrogen and charged with 157 grams (0.5 mole) of eicosylphosphine and 54 grams (0.5 mole) of redistilled 1,5-cyclooctadiene. A nitrogen blanket was maintained and the reactants brought to 135°C by immersion in an oil bath. A sample was removed and its infrared spectrum recorded. Then a solution of 4 grams (0.025 mole) of di(tert-butyl) peroxide in 15 ml of n-decane was added dropwise over a period of one hour. The reaction was exothermic and the temperature was maintained at 135—145°C by temporarily lowering the oil bath. After addition of the catalyst, the mixture was heated for one hour at 150°C. The olefinic band at 6.05 μ had then disappeared. Heating for one additional hour had no effect on residual P—H absorbance. Claisen distillation of the reaction mixture using steam in the condenser jacket gave 20 grams of unreacted eicosylphosphine, b.p. 164—210°C at 0.8 mm, and 155 grams of a mixture of 9-eicosyl-9-phosphabicyclo[4.2.1]nonane and 9-eicosyl-9-phosphabicyclo[3.3.1]nonane, b.p. 230—238°C at 0.3 mm (m.p. 38—39°C). The pot residue weighed 22 grams, representing 87% conversion of reactants to desired product in 84% yield.

Analysis: Calculated for $C_{24}H_{44}P$: C 79.6; H 13.1; P 7.3;

Basicity 0.24 eq/100 g.

Found: C 79.8; H 13.2; P 7.3;

Basicity 0.23 eq/100 g.

EXAMPLE XIII

A mixture of 162 grams (1.5 moles) of redistilled 1,5-cyclooctadiene, 100 ml of deaerated pentane, and 12.3 grams (0.075 mole) of azobisisobutyronitrile was charged to a 700 ml pressure vessel. The vessel was closed, cooled to -80°C in a dry-ice bath and evacuated. Nitrogen was bled in and the process repeated twice more in order to remove oxygen. 52 grams (1.5 moles) of phosphine were then charged to the evacuated vessel by means of a weighed transfer bomb. The vessel was then gently heated to 75°C, at which temperature the pressure was 275 psig. After 20 minutes at 75°C, exothermic increase to 85°C occurred accompanied by a pressure drop. One hour after the initial reaction had commenced, the pressure remained steady at 115 psig. Heating at 75°C was continued for a total of 12 hours. The vessel was again quenched in dry ice, evacuated, and nitrogen bled in. The contents were then transferred under a blanket of nitrogen to a distillation flask, the vessel being rinsed with degassed pentane. The solvent was removed by distillation under nitrogen, the kettle temperature being taken to 90°C. The crude product weighed 211 grams. Sublimation from an oil bath at 100°C and 0.3 mm gave 120 grams (57%) of a mixture of 9-phosphabicyclo[4.2.1]nonane and 9-phosphabicyclo[3.3.1]nonane, m.p. 117°C.

Analysis: Calculated for $C_8H_{13}P$: C 67.6; H 10.6; P 21.8;

Found: C 66.9; H 10.8; P 21.2.

Gas chromatographic analysis of this product demonstrated the presence of two closely eluted isomers, 9-phosphabicyclo[4.2.1]nonane and 9-phosphabicyclo[3.3.1]nonane, in the ratio of 0.55:1.

EXAMPLE XIV

Cobalt catalysts containing cobalt in complex combination with carbon monoxide and the below-indicated tertiary phosphine ligands were utilized with 1-dodecene as olefin. The catalysts were prepared *in situ*, in the equipment to be described, from cobalt octanoate.

The reactor was a 300 ml stainless steel magnetically stirred autoclave operated at 1250 rpm and connected to a source of a premixed hydrogen-carbon monoxide gas delivered at any desired constant pressure. The components forming the catalyst (e.g. tertiary phosphine and cobalt octanoate) and the olefin, 1-dodecene, were charged to the reactor; the reactor was closed, evacuated, and pressured with H_2 -CO gas until all foreign gases were displaced. The reactor was then heated under sufficient H_2 + CO pressure so that the final pressure at reaction temperature was about 1000 psig. After the temperature was equilibrated, the pressure reduction was recorded. The reaction conditions and results are tabulated in Table III.

Example XV below, utilizing the commercially available tri-n-butylphosphine as the phosphorus ligand, was taken as a comparative control. A comparison between Example XV and Examples XVI—XXIII shows that the quantity of undesirable

saturated hydrocarbon by-product formed when using as ligands the tertiary, six-membered heterocyclic phosphines of the invention is less by a factor of about one-third to two-thirds, averaging about one-half, than that formed when using tri-n-butylphosphine, in spite of the fact that the hydrogenating activity of the novel catalysts in Examples XVI—XXIII was sufficient to ensure essentially complete hydrogenation of the intermediate aldehyde.

TABLE III

Hydroformylation of 1-Dodecene

Example	Phosphine ligand	Cobalt wt. %	Phosphine/cobalt mole ratio	H ₂ /CO mole ratio	Temperature, °C.	Pressure, atm.	Time required for 50% conversion min.	Conversion of 1-dodecene, %	Conversion to saturated hydrocarbon, %	Conversion to primary alkanols, %
XV	Tri-n-butylphosphine	0.2	2	2.1	198—202	68	36	99.1	20.4	78.2
XVI	1-Phenylphosphorinane	0.2	2	2.1	198.5—202.5	68	23	100	10.7	88.8
XVII	1-(2,4,4-Trimethyl-1-pentenyl)phosphorinane	0.2	3	2.1	200.5—203	68	24	99.0	8.4	90.1
XVIII	1-Eicosylphosphorinane	0.2	4	2.1	200	81.6	28	98.9	8.9	87.5
XIX	2,2,6,6-Tetramethyl-1-phenylphosphorinane	0.2	4	2.1	200	68	22	99.2	7.4	91.2
XX	2,2,6,6-Tetramethyl-1-octadecylphosphorinane	0.2	2	2.1	198—200	81.6	38	100	10.3	89.1
XXI	1-Diisopropylamino-phosphorinane	0.2	2	2.1	198—202	81.6	29	98.4	13.2	84.8
XXII	2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinane	0.2	4	2.1	198—200	68	64	99.2	11.5	87.1
XXIII	4,4-Dimethyl-1-phenylphosphorinane	0.2	2	2.1	198—200	81.5	27	98.3	10.9	87.3

EXAMPLE XXIV (for comparison only)

5 1-Dodecene was hydroformylated in the manner described in the previous examples by reaction with carbon monoxide and hydrogen in a H_2/CO mole ratio of 2:1, at 198—203°C, a pressure of 68 atmospheres, with a contact time of 30 hours in the presence of a catalyst consisting of triphenylphosphine-cobalt-carbonyl. There was obtained a conversion of 98.8% of the olefin with a selectivity to C_{13} alcohols of 86.1%. Of the C_{13} alcohols obtained, 52% was the linear, straight-chain n-tridecanol, the remainder branched-chain alcohols. 5

EXAMPLE XXV

10 Similarly 1-dodecene was hydroformylated by reaction with carbon monoxide and hydrogen in a H_2/CO mole ratio of 2:1, at 198—201°C, a pressure of 68 atmospheres, with a contact time of three hours in the presence of a novel catalyst consisting of 1-phenylphosphorinane-cobalt-carbonyl. There was obtained a conversion of the olefin of 99.6%, with a selectivity to C_{13} alcohols of 86.9%. Of the C_{13} alcohols obtained, 77% was the linear, straight-chain n-tridecanol, the remainder branched-chain alcohols. 15

EXAMPLE XXVI

20 Similarly, 1-dodecene was hydroformylated by reaction with carbon monoxide and hydrogen in a H_2/CO mole ratio of 2:1, at 200°C, a pressure of 81.6 atmospheres, with a contact time of five hours in the presence of a novel catalyst consisting of 1-eicosyl-phosphorinane-cobalt-carbonyl. There was obtained a conversion of the olefin of 99.4%, with a selectivity to C_{13} alcohols of 83.3%. Of the C_{13} alcohols obtained, 80% was the linear straight-chain n-tridecanol, the remainder branched-chain alcohols. 20

25 It is seen from the foregoing results that with triphenylphosphine as the phosphorus ligand of the catalyst the predominance of the highly desirable linear straight-chain or normal alcohol over the branched-chain isomers is not so great as with the novel catalyst in which the phosphorus ligands are the tertiary six-membered heterocyclic phosphines of the invention. 25

EXAMPLES XXVII—XXXI

30 In Table IV experimental results and reaction conditions are collected illustrating the hydroformylation of 1-dodecene with 7-membered heterocyclic phosphine containing catalysts. 30

TABLE IV
Hydroformylation of 1-Dodecene

Example	Phosphine ligand	Cobalt wt. %	Phos- phine co- balt mole ratio	H ₂ /CO mole ratio	Temper- ature. °C.	Pres- sure, atm.	Time re- quired for 50% con- version, min.	Con- version of 1- dodecene %	Conversion to	
									saturated hydro- carbon, %	primary alkanols, %
XXVII	1-Phenylphosphane	0.2	2	2.1	198—200	81.6	24	100	13.1	86.0
XXVIII	3,6-Dimethyl-1-(1-methyl- hepta-decyl)phosphane	0.2	2	2.1	198—200	81.6	33	97.8	15.0	82.6
XXIX	1-Eicosyl-3,6-dimethyl- phosphane	0.2	1.5	2.1	198—200	81.6	28	97.8	15.7	80.7
XXX	3,6-Dimethyl-1-phenyl- phosphane	0.2	2	2.1	200	81.6	22	100	12.7	86.2
XXXI	3,6-Dimethyl-1-octadecyl- phosphane	0.2	2	2.1	198—200	81.6	26	98.4	16.6	81.7

EXAMPLE XXXII

1-dodecene was hydroformylated by reaction with carbon monoxide and hydrogen in a H_2/CO mole ratio of 2:1, at $200^\circ C$, a pressure of 81.6 atmospheres, with a contact time of three hours in the presence of a novel catalyst consisting of 3,6-dimethyl-1-phenylphosphhepane-cobalt-carbonyl. There was obtained a conversion of the olefin of 100%, with a selectivity to C_{13} alcohols of 86.2%. Of the C_{13} alcohols obtained, 74.4% was the linear, straight-chain n-tridecanol, the remainder branched-chain alcohols.

EXAMPLE XXXIII

Similarly, 1-dodecene was hydroformylated by reaction with carbon monoxide and hydrogen in a H_2/CO mole ratio of 2:1, at $198-200^\circ C$, a pressure of 81.6 atmospheres, with a contacting time of three hours in the presence of a novel catalyst consisting of 3,6-dimethyl-1-octadecyl-phosphhepane-cobalt-carbonyl. There was obtained a conversion of the olefin of 98.4% with a selectivity to C_{13} alcohols of 81.7%. Of the C_{13} alcohols obtained, 82% was the linear straight-chain n-tridecanol, the remainder branched-chain alcohols.

EXAMPLE XXXIV

In a similar way an experiment was carried out, using a bicyclic heterocyclic phosphine containing catalyst. Results of this experiment as well as reaction conditions are given below:

Phosphine Ligand	Mixture of 9-phenyl-9-phosphabicyclo[4.2.1]nonane and 9-phenyl-9-phosphabicyclo[3.3.1]nonane
Cobalt, % wt.	0.2
Phosphine/Cobalt mole ratio	2
H_2/CO mole ratio	2.1
Temperature, $^\circ C$.	198—200
Pressure, atm.	81.6
Time required for 99% conversion, hr.	1.5
Conversion of 1-dodecene, %	100
Conversion to saturated hydrocarbon, %	11.8
Conversion to primary alkanols, %	87.6

EXAMPLE XXXV

Similarly to the experiment described in Example XXXIV 1-dodecene was hydroformylated by reaction with carbon monoxide and hydrogen in a H_2/CO mole ratio of 2:1, at $183^\circ C$, a pressure of 68 atmospheres, with a contact time of 6 hours in the presence of a novel catalyst consisting of a mixture of 9-eicosyl-9-phosphabicyclo[4.2.1]nonane-cobalt-carbonyl and 9-eicosyl-9-phosphabicyclo[3.3.1]nonane-cobalt-carbonyl at a phosphine/cobalt mole ratio of 1.5:1. There was obtained a conversion of the olefin of 98.5% with a selectivity to C_{13} alcohols of 86.9%. Of the C_{13} alcohols obtained, 89% was the linear, straight-chain n-tri-decanol, the remainder branched-chain alcohols.

It is seen from the foregoing results that with triphenylphosphine as the phosphorus ligand of the catalyst the predominance of the highly desirable linear straight-chain or normal alcohol over the branch-chain isomers is not so great as with the novel catalyst in which the phosphorus ligand is the bicyclic heterocyclic tert-phosphine of the invention.

EXAMPLE XXXVI (for comparison only)

1-dodecene was hydroformylated in the manner described in the previous examples with the addition that alkali was added in a $KOH/cobalt$ mole ratio of 0.75:1. By

reaction with carbon monoxide and hydrogen in a H_2/CO mole ratio of 2:1, at 200—203°C, a pressure of 68 atmospheres, with a contact time of 5.5 hours in the presence of a catalyst consisting of trilaurylphosphine-cobalt-carbonyl at a phosphine/cobalt mole ratio of 1.5:1, there was obtained a conversion of 99.2% of the olefin with a conversion to primary C_{13} alcohols of 83.2%.

EXAMPLE XXXVII

Similarly 1-dodecene was hydroformylated at 183—185°C with a contact time of six hours in the presence of a novel catalyst consisting of a mixture of 9-eicosyl-9-phosphabicyclo[4.2.1]nonane-cobalt-carbonyl and 9-eicosyl-9-phosphabicyclo[3.3.1]nonane-cobalt-carbonyl. There was obtained a conversion of 98.5% of the olefin with a conversion to primary C_{13} alcohols of 86.9%.

EXAMPLE XXXVIII

Similarly 1-dodecene was hydroformylated at 185°C with a contact time of five hours at a pressure of 81.6 atmospheres in the presence of a novel catalyst consisting of a mixture of 9-phenyl-9-phosphabicyclo[4.2.1]nonane-cobalt-carbonyl and 9-phenyl-9-phosphabicyclo[3.3.1]nonane-cobalt-carbonyl. There was obtained a conversion of 99.4% of the olefin with a conversion to primary C_{13} alcohols of 88.2%.

The foregoing results of obtaining a similar conversion at about the same contact time but at approximately 15°C lower temperature demonstrate the exceptionally rapid rate of hydroformylation achieved by the new and improved hydroformylation catalyst in which the phosphorus ligands are the bicyclic heterocyclic tert-phosphines of the invention as compared with the rate achieved when a trialkylphosphine such as trilaurylphosphine is the phosphorus ligand of the catalyst.

EXAMPLE XXXIX

1-dodecene was hydroformylated in the manner described in Example XXXVIII by reaction with carbon monoxide and hydrogen in a H_2/CO mole ratio of 2:1, at 163—165°C, a pressure of 81.6 atmospheres, with a contact time of 11 hours in the presence of a catalyst consisting of 9-phenyl-9-phosphabicyclo[3.3.1]nonane-cobalt-carbonyl at a phosphine/cobalt mole ratio of 1.5:1. There was obtained a conversion of the olefin of 95% with a conversion to primary C_{13} alcohols of 83.4%. Of the C_{13} alcohols obtained, 87.6% was the linear, straight-chain n-tridecanol.

EXAMPLE XXXX

1-dodecene was hydroformylated in the manner described in Example XXXVIII by reaction with carbon monoxide and hydrogen in a H_2/CO mole ratio of 2:1, at 183—185°C, a pressure of 81.6 atmospheres, with a contact time of 6 hours in the presence of a catalyst consisting of a mixture of 9-eicosyl-9-phosphabicyclo[4.2.1]nonane-cobalt-carbonyl and 9-eicosyl-9-phosphabicyclo[3.3.1]nonane-cobalt-carbonyl at a phosphine/cobalt mole ratio of 1.3:1. There was obtained a conversion of the olefin of 98.5% with a conversion to primary C_{13} alcohols of 86.9% and to by-product saturated hydrocarbon of 11.6%. Repetition of this example with a decrease in pressure to 600 psig and slight increase in contact time to seven hours yielded a conversion about equal to that obtained at the higher pressure, 98.4% of the olefin, 86.6% to primary C_{13} alcohols and 11.7% to by-product saturated hydrocarbon.

EXAMPLE XXXXI

A series of internal normal olefins was prepared by chlorination of straight-chain paraffins followed by dehydrochlorination to a corresponding mixture of substantially internal olefins containing less than 5% of the 1-olefin. By this method internally unsaturated tetradecenes, internally unsaturated tridecenes, internally unsaturated dodecenes, and internally unsaturated undecenes were each prepared. Each of these internal olefins was hydroformylated in the manner described in Example XXXVIII by reaction with carbon monoxide and hydrogen in a H_2/CO mole ratio of 2:1, at 170°C, a pressure of 81.6 atmospheres, with a contact time of 7.5 to 9 hours in the presence of a catalyst consisting of a mixture of 9-eicosyl-9-phosphabicyclo[4.2.1]nonane-cobalt-carbonyl and 9-eicosyl-9-phosphabicyclo[3.3.1]nonane-cobalt-carbonyl at a weight % cobalt of 0.4 and a phosphine/cobalt mole ratio of 2:1. The results are tabulated in Table V, demonstrating the effectiveness of the novel catalysts to convert internal normal olefins to a substantial quantity of normal terminal alcohols.

TABLE V

Hydroformylation of Internal Olefins

Internal olefin	Conversion of olefin, %	Conversion to primary alkanols, %	Linear, straight-chain alkanol, %
Tetradecene	98.6	83.1	n-pentadecanol, 84.0
Tridecene	96.5	84.2	n-tetradecanol, 86.6
Dodecene	95.9	86.7	n-tridecanol, 87.5
Undecene	95.5	82.4	n-dodecanol, 89.7

A further economic advantage obtainable with the catalysts of the present invention is that, in continuous hydroformylation processing, longer catalyst life is achieved by virtue of the ability to hydroformylate at lower temperatures. Additionally, these catalysts are more stable during the hydroformylation process owing to the fact that their resistance to oxidation and degradation is higher than that of catalysts having a trialkylphosphine ligand.

EXAMPLE XXXXII

In an analogous way as described in the previous Examples an experiment has been performed using an unsaturated bicyclic heterocyclic phosphine containing catalyst. Reaction conditions and results are given below.

Phosphine ligand	9-phenyl-9-phosphabicyclo-[4.2.1]nona-2,4,7-triene
Cobalt, % wt.	0.2
Phosphine/cobalt mole ratio	2
H ₂ /CO mole ratio	2.1
Temperature, °C.	198—200
Pressure, atm.	81.6
Time required for 99% conversion, hr.	1.5
Conversion of 1-dodecene, %	98.6
Conversion to saturated hydrocarbon, %	9.6
Conversion to primary alkanols, %	88.6

EXAMPLE XXXXIII

1-dodecene was hydroformylated by reaction with carbon monoxide and hydrogen in a H₂/CO mole ratio of 2:1, at 200°C, a pressure of 81.6 atmospheres, with a contact time of 1.3 hours in the presence of a novel catalyst consisting of 9-phenyl-9-phosphabicyclo[4.2.1]-nona-2,4,7-triene-cobalt-carbonyl at a phosphine/cobalt mole ratio of 1.5:1. There was obtained a conversion of the olefin of 98.6% with a selectivity to C₁₃ alcohols of 88.6%. Of the C₁₃ alcohols obtained, 68% was the linear, straight-chain n-tridecanol, the remainder branched-chain alcohols.

EXAMPLE XXXXIV

In a similar way as has been described in Example XXXVI 1-dodecene was

hydroformylated at 175°C with a contact time of five hours at a pressure of 81.6 atmospheres in the presence of a novel catalyst consisting of 9-phenyl-9-phosphabicyclo-[4.2.1]-nona-2,4,7-triene-cobalt-carbonyl. There was obtained a conversion of 98.6% of the olefin with a conversion to primary C₁₁ alcohols of 88.6%.

The foregoing results of obtaining a similar conversion at about the same contact time but at approximately 25°C lower temperature demonstrate the exceptionally rapid rate of hydroformylation achieved by the new and improved hydroformylation catalyst in which the phosphorus ligands are the hydrocarbyl-substituted monophosphabicyclononatrienes of the invention as compared with the rate achieved when a trialkylphosphine such as triaurylphosphine is the phosphorus ligand of the catalyst.

A further economic advantage obtainable with the catalysts of the present invention is that, in continuous hydroformylation processing, longer catalyst life is achieved by virtue of the ability to hydroformylate at lower temperatures. Additionally, these catalysts are more stable during the hydroformylation process owing to the fact that their resistance to oxidation and degradation is higher than that of catalysts having a trialkylphosphine ligand.

WHAT WE CLAIM IS:—

1. A process for the preparation of an aldehyde and/or alcohol by reaction of an olefinic compound with carbon monoxide and hydrogen in the presence of a complex catalyst comprising cobalt, carbon monoxide and a heterocyclic phosphine, in which a heterocyclic group with at least five carbon atoms is present.

2. A process as claimed in claim 1, in which the catalyst contains a tertiary heterocyclic phosphine of the said category.

3. A process as claimed in claim 2, in which the catalyst contains a tertiary 6-membered mono-heterocyclic phosphine.

4. A process as claimed in claim 3, in which in the phosphine the phosphorus atom is attached to a 1,5-hydrocarbylene diradical containing from 5 to 33 carbon atoms, such that any hydrocarbon substituent attached to a bridge carbon atom of said diradical contains no more than ten carbon atoms, and to a substituted or unsubstituted hydrocarbyl radical containing from 4 to 36 carbon atoms.

5. A process as claimed in claim 4, in which the phosphine is 2,2,6,6-tetramethyl-1-phenylphosphorinane.

6. A process as claimed in claim 4, in which the phosphine is 1-eicosylphosphorinane.

7. A process as claimed in claim 4, in which the phosphine is 1-(2,4,4-trimethyl-1-pentenyl)phosphorinane.

8. A process as claimed in claim 4, in which the phosphine participant is 1-diisopropylaminophosphorinane.

9. A process as claimed in claim 2, in which the catalyst contains a tertiary 7-membered mono-heterocyclic phosphine.

10. A process as claimed in claim 9, in which in the phosphine the phosphorus atom is attached to a 1,6-hydrocarbylene diradical containing from 6 to 34 carbon atoms, such that any hydrocarbon substituent attached to a bridge carbon atom of said diradical contains no more than ten carbon atoms, and to a hydrocarbyl radical containing from 4 to 36 carbon atoms.

11. A process as claimed in claim 10, in which the phosphine is 1-phenylphosphene.

12. A process as claimed in claim 10, in which the phosphine is 3,6-dimethyl-1-phenylphosphene.

13. A process as claimed in claim 2, in which the phosphine is a bicyclic heterocyclic tertiary phosphine.

14. A process as claimed in claim 13, in which the phosphine is a hydrocarbyl-substituted mono-phosphabicyclo hydrocarbon having 8 or 9 ring atoms including the phosphorus atom in which the smallest phosphorus-containing ring contains at least 5 atoms and the phosphorus atom is not a bridgehead atom.

15. A process as claimed in claim 14, in which the bicyclic heterocyclic structure of the phosphine contains no more than two alkyl substituents each containing from 1 to 4 carbon atoms, and being attached to different ring carbon atoms.

16. A process as claimed in claim 14 or 15, in which the monophosphabicyclic hydrocarbon contains from 12 to 40 carbon atoms.

17. A process as claimed in any of claims 13—15, in which the phosphine is 9-

eicosyl-9-phosphabicyclo[4.2.1]nonane and/or 9-eicosyl-9-phosphabicyclo[3.3.1]-nonane.

18. A process as claimed in any of claims 13—15, in which the phosphine is 9-phenyl-9-phosphabicyclo[4.2.1]nonane and/or 9-phenyl-9-phosphabicyclo[3.3.1]-nonane. 5
19. A process as claimed in claim 13 or 14, in which the phosphine is a hydrocarbyl-substituted monophosphabicyclic-nonatriene.
20. A process as claimed in claim 19, in which the phosphine contains from 12 to 38 carbon atoms. 10
21. A process as claimed in claim 20, in which the phosphine is 9-eicosyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene.
22. A process as claimed in claim 20, in which the phosphine is 9-phenyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene.
23. A process as claimed in any of claims 1—22, in which a reaction temperature between 100 and 300°C is used. 15
24. A process as claimed in claim 23, in which the reaction temperature is in the range from 125 to 210°C.
25. A process as claimed in any of claims 1—24, in which the reaction is performed under a pressure in the range from 20.4 to 102 atmospheres. 20
26. A process as claimed in claim 25, in which the pressure is in the range from 27.2 to 81.6 atmospheres.
27. A process for the preparation of an aldehyde and/or alcohol, substantially as described in any of Examples XVI—XXIII, XXV—XXXV, XXXVII—XXXXIV.
28. An aldehyde or alcohol, whenever prepared by a process as claimed in any of claims 1—27. 25
29. A process for the preparation of a complex suitable to be used as a catalyst in the process as claimed in any of claims 1—27, in which a cobalt salt is complexed with a heterocyclic phosphine in which a heterocyclic group with at least five carbon atoms is present. 30
30. A process as claimed in claim 29, in which the cobalt salt is a cobalt alkanoate having 6 to 12 carbon atoms in the molecule.
31. A complex whenever prepared by a process as claimed in claim 29 or 30.
32. A process for the preparation of a heterocyclic tertiary phosphine having at least five carbon atoms in the heterocyclic group and suitable to be used as participants in catalysts in the process as claimed in any of claims 2—12 or 23—27, in which a divinyl-substituted hydrocarbon containing two non-conjugated double bonds, separated by a hydrocarbylene group of 1 to 14 carbon atoms, the bridge connecting said double bonds comprising one or two carbon atoms, is reacted with a mono-substituted phosphine in the presence of a free radical-generating catalyst and in the absence of substantial amounts of oxygen. 35
33. A process as claimed in claim 32, in which the divinyl-substituted hydrocarbon is 1,4-pentadiene, biallyl or bimethallyl. 40
34. A process for the preparation of a monocyclic 6- or 7-membered heterocyclic phosphine substantially as described in any of Examples I—VII.
35. A heterocyclic tertiary phosphine when prepared by a process as claimed in any of claims 32—34. 45
36. As a novel compound, a bicyclic heterocyclic secondary or tertiary phosphine.
37. A monophosphabicyclic hydrocarbon having from 7 to 46 carbon atoms, in which bicyclic structure the phosphorus atom is a member of a ring, without being a bridgehead atom, and the smallest phosphorus-containing ring consists of at least 5 atoms. 50
38. A monophosphabicyclic hydrocarbons as claimed in claim 37 in which the phosphorus atom is attached to a hydrocarbyl substituent from 1 to 36 carbon atoms.
39. 9-Phosphabicyclononanes. 55
40. 9-Phosphabicyclo[4.2.1]nonane.
41. 9-Phosphabicyclo[3.3.1]nonane.
42. 9-Phenyl-9-phosphabicyclo[4.2.1]nonane.
43. 9-Phenyl-9-phosphabicyclo[3.3.1]nonane.
44. 9-Eicosyl-9-phosphabicyclo[4.2.1]nonane.
45. 9-Eicosyl-9-phosphabicyclo[3.3.1]nonane. 60
46. A process for the preparation of a bicyclic heterocyclic secondary and tertiary phosphines, suitable to be used as a participant in a catalyst in the process as claimed in any of claims 1, 2 and 13—27, in which a cyclic hydrocarbon containing two ring

non-conjugated and non-homoconjugative double bonds is reacted with PH_3 or a mono-substituted phosphine in the presence of a free radical-generating catalyst and in the substantial absence of oxygen.

5 47. A process as claimed in claim 46, in which substantially equimolar amounts of cyclic hydrocarbon having 7 or 8 ring carbon atoms and containing two non-conjugated and non-homoconjugative double bonds is reacted with PH_3 or a mono-substituted phosphine containing from 4 to 30 carbon atoms in the presence of a free radical generating catalyst and in the substantial absence of oxygen. 5

10 48. A process as claimed in claim 46 or 47, in which the cyclic hydrocarbon is 1,5-cyclooctadiene or 3,7-dimethyl-1,5-cyclooctadiene. 10

49. A process for the preparation of a monophosphabicyclic hydrocarbon, substantially as described in any of Examples VIII—XIII.

50. A bicyclic heterocyclic phosphine when produced by a process as claimed in any of claims 44—49.

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